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13. ABSTRACT (Maximum 200 words)

This report summarizes efforts and accomplishments relative to modeling of the mechanical alloying procesing and in synthesis and consolidation of structural materials made by mechanical alloying. Models depicting the extent of deformation and the fracture and welding frequencies of powders subjected to mechanical alloying are encapsulated. A description of an improved attritor processing scheme is given. In addition, we describe the means of synthesizing nanocermets of the Cu-NbC system. The structure and properties of these materials are described, as they are know at this time. Finally, a description of consolidated heavy metals and their properties as they are found when prepared from mechanically alloyed precursor powders is given.

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MECHANICAL ALLOYING PROCESSING WITH APPLICATIONS TO STRUCTURAL MATERIALS

FINAL REPORT

T. H. COURTNEY

SEPTEMBER, 1994

U. S. ARMY RESEARCH OFFICE

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FINAL REPORT: MECHANICAL ALLOYING PROCESSING WITH APPLICATION TO STRUCTURAL MATERIALS

RESEARCH AGREEMENT NO. DAAH04-93-G-0057

OVERVIEW

This report is a summary of work performed on this program for the period November, 1992 - July, 1994. It also summarizes the research of Mr. Robert Comstock, a student supported by an AASERT supplement to the grant. The report capsulizes work that has been published, either in archival journals or in conference proceedings, emphasizing the more important ramifications of the published work. More detailed descriptions are provided for research that has not yet been published.

The report is divided into two general technical areas; modeling of mechanical alloying (MA) and synthesis devolving on MA. Synthesis includes both material synthesis by MA and consolidation of the resulting powders into a form suitable for potential engineering use. Some properties of consolidated materials are also presented.

PROGRAM GOALS

The long term goal of this program is to use the MA process to synthesize technologically useful structural materials. To do this, understanding of the essential physics as well as some of the subtleties of this process is required. Thus we have conducted modeling studies aimed at furthering our comprehension of MA dynamics in addition to executing empirical studies dealing with synthesis, consolidation and properties. The report separately describes activities in these two broad areas.

MODELING STUDIES

Our modeling studies have been well-received. We have been requested to, and have submitted, three review articles on the topic and a fourth is in preparation.[1] We have classified our modeling of MA into two categories; local modeling and global modeling. Local modeling aims to define the conditions for particle fracture and welding during a "typical" grinding media collision, and to ascertain the deformation the powder particles experience in such a collision. Such a collision "snapshot" can be incorporated into a computational scheme Having capability for providing a temporal description of the process. This type of modeling is most useful for process control and optimization. In short, if the model is correct in its essentials "experiments" - which define the role of process variables on process efficiency and

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[1] - See Appendix B for a list of publications supported by the grant. The three review articles in the list are papers 11, 12 and 18. The additional paper - for a special edition of the Transactions of The Japan Institute of Metals - is in preparation.

the properties of processed powder - can be conducted by simulation, thereby reducing considerably the time, effort and cost associated with extensive empirical studies.

Local modeling is a topic of papers 5, 6, 8, 13, 14 and 17 (Appendix B) as well as a topic of the above-noted review papers. In brief, papers 5 and 6 represent a phenomenological approach to local modeling, whereas papers 8, 13 and 14 represent efforts along the lines just described. Paper 8 defines criteria for powder particle deformation, cold-welding and fracture in a single collision. Effort was taken to keep the model as simple as possible, subject to the critical constraint of physical plausibility. Papers 13 and 14 describe the computational development of the model and some of its implementations. The model correctly predicts the trends in development of powder particle size, microstructural refinement and hardness during milling. "Exact" predictions are not had. (Given the complexity of the process, they ought not to be expected.) For example, predicted particle sizes are correct to better than a factor of two, and the milling times at which these sizes are observed are within a factor of two or so to those experimentally found. Since the "trends" of measurable powder characteristics are predicted by the model, the predictions can be adjusted with recourse to a small number of empirical adjustments. This is in contrast to the large number of experiments that would have to be conducted absent the model. The programs we have developed - termed MAP1 and MAP2 - will be made available to the scientific community through publication of papers 13 and 14. Because of the "grapevine", the programs have already "gotten around." For example, ALCOA Laboratories has the programs and are using them in their MA studies.

Global modeling considers characteristics of a specific MA device. Global modeling is concerned with improving device efficiency and with empirical extraction of appropriate values for the process variables used in local modeling. The most widely cited of our global studies is paper 4 (Appendix B). In this work, high speed cinematography was used to investigate attritor media dynamics. Slow motion viewing of the film and frame-by-frame analysis of it allowed classification of different regions of the attritor on the basis of the prevalent type of impact taking place in the regions. Powder distribution within the attritor was also studied. It was found that powder substantially segregates to the least "dynamic" attritor region. The video we made, which summarized these studies, is available for general use. We have had about a dozen or so requests for the video, including one from the primary attritor manufacturer in the United States.

As a result of this study, several suggestions for improving attritor efficiency were made. One was to use differently sized balls in the attritor (the prevalent practice is to use balls of the same size). The reasoning behind the suggestion is that the balls assume a close-packed array when balls of the same size are employed. The array mitigates energetic ball-ball collisions, the ones believed most effective for MA. It was suggested that a mixture of differently sized balls would disrupt the close-packed array, thus facilitating more energetic media collisions.

Timothy Cook pursued this idea in his recently completed M.S. thesis. Cook used a variety of differently sized balls (of differing number fractions) in the attritor and, using high speed cinematography, studied their dynamics. At low rotational velocities, the small balls segregate to the tank bottom. They begin to mix as the rotational velocity is increased until, at a critical velocity which is dependent on ball diameter ratio and small ball number fraction, "complete" mixing occurs. When it does the close-packed array is disrupted. "Substitutional" or "interstitial" defects are formed (depending on the ball diameter ratio); "edge dislocations" are also occasionally observed.

Using several ball size combinations[2,] Cook investigated alloying kinetics of Cu and Nb. These were compared to alloying kinetics when milling with only one size ball. Alloying rates were ascertained by measurement of the milling time variation of powder particle numbers. In the initial stages of MA, these numbers decrease since particle welding takes place at a rate greater than particle fracture. At longer milling times the opposite holds. Cook's results are shown in Fig. 1. We note that the logarithmic coordinates employed in the figure minimize the very real effect that the use of differently sized balls has on alloying kinetics. In effect, the net particle welding rate (i.e., the difference between the respective welding and fracture rates) is essentially doubled in the welding dominant stage of MA (the first 4 hr. of milling). This is reflected by an approximate factor of two decrease in particle numbers after 4 hr of milling with differently sized balls. In addition, the net fracture rate for milling times greater than 4 hr is also about doubled when differently sized balls are employed. This is indicated by the approximate doubling of the rate of increase in particle numbers in this alloying stage. The effect is confirmed by metallographic observations of milled powders. The microstructural scale in powders milled with differently sized balls is finer.

In an independent undergraduate study, Mr. Larry Henley has investigated the dynamics of a transparent ball mill. Ball mills are the primary tool for mass production of mechanically alloyed powders. Ball mills, of course, are also used for many mineral engineering processes. Most of Henley's results have confirmed what is known from the extant mineral engineering literature. However, one noteworthy and new finding of his is that balls are displaced along the longitudinal axis of the mill as well as being rotated about this axis. The longitudinal motion enhancesa ball circulation in the mill, and we suspect it improves process efficiency. Ball mills are operated at an intermediate rotational velocity, one that permits ball rotation about the mill axis but does not result in balls being pinned to the mill wall. Henley has found that the usable rotational velocity range depends on the mill's length to diameter ratio. We believe this is related to the longitudinal circulation of the balls within the mill, but have not yet defined this relationship.

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[2] - The ball size combinations and respective number fractions used are not necessarily the optimum ones insofar as improving process efficiency is concerned.
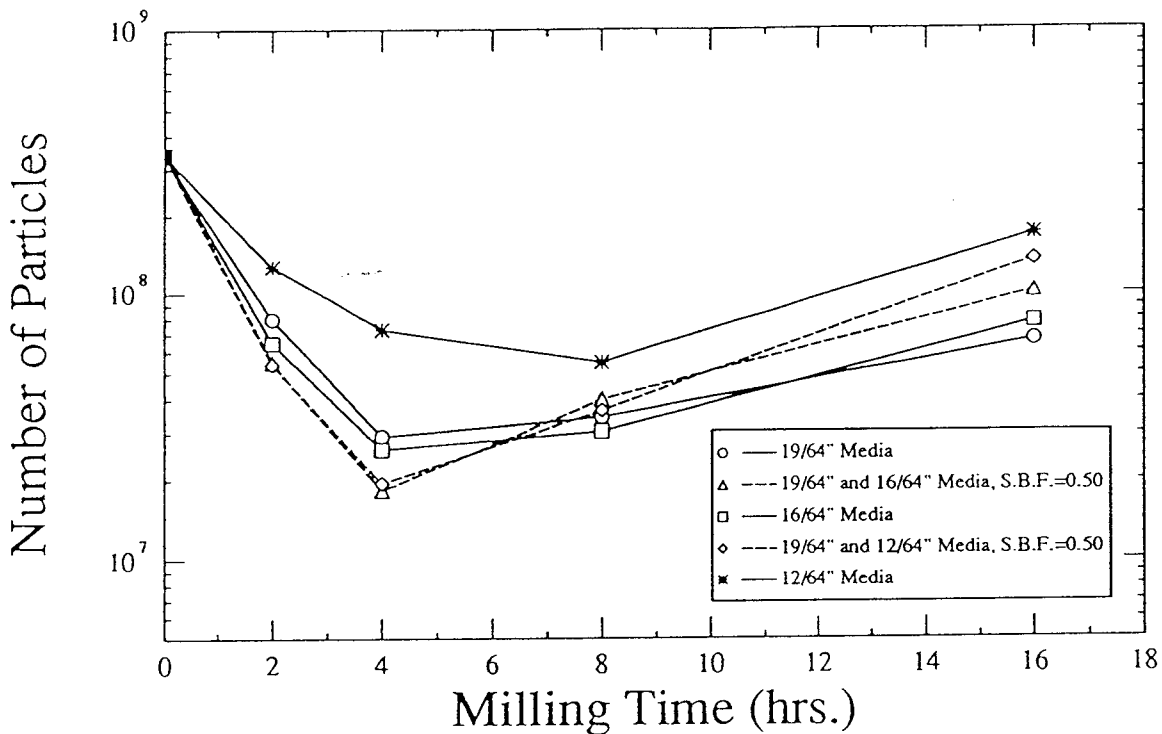
Figure 1: Number of powder particles in mill as a function of attritor milling time when milling with the same size balls and differently sized balls. Use of different sized balls approximately doubles the initial net particle welding rate in the first 4 hr. of milling, as indicated by a lesser number of particles (by about a factor of two) when differently sized balls are employed. Similarly, in the fracture dominant regime of alloying (milling times greater than about 4 hr.) the net fracture rate is about doubled when differently sized balls are used, as indicated by the doubling in the rate of increase in particle sizes for times in excess of 4 hr. The "anomalous" behavior exhibited by use of balls of 12/64" diameter is a result of an increase in the "dead zone" of the attritor when progressively smaller balls of the same diameter are used for attrition milling.

Our computationa simulations of local modeling and our attempt to link local with global modeling are not yet completed. Dr. Maurice and Prof. Courtney are collaborating on two papers in this vein (these are not listed in Appendix B as they have not yet been submitted). The papers deal with: distributions in energy dissipation for media collisions in a SPEX mill; comparison of the global dynamics of an attritor and a SPEX mill; and, with the aid of MAP1 and MAP 2, a series of "thought" experiments that clarify the role of material and process variables on MA efficiency. In addition, a third program, MAP3, has been developed by Maurice. It mimics a harmonic oscillator MA device. This simulation has some relevance to a SPEX mill. It has even more relevance to certain types of mills used primarily in Europe for MA.

MATERIALS SYNTHESIS, CONSOLIDATION AND PROPERTIES

Our experimental studies dealing with synthesis, consolidation and properties have focused on three material systems; Cu-Nb, Cu-NbC and W heavy metals (W-Ni-Fe alloys). The Cu-Nb system is a useful model system in several respects. The elements are insoluble, so metallographic examination of processed powders can "track" alloying kinetics and microstructural evolution (e.g., Cook's M.S. thesis and papers 6 and 7, Appendix B). In addition, Cu-Nb has potential as a high strength- high conductivity material.

A technological concern relative to mechanically alloyed powders is their nonequilibrium nature. That is, the intensive powder deformation accompanying the process yields fine, often nanocrystalline, structures. In addition, amorphous structures are often formed and extended solubility is common. Properties of the nonequilibrium structures are often intriguing. Maintaining them during consolidation is a challenge. The Cu-Nb system is useful for studying the ways by which microstructure is altered during consolidation (papers 1, 10 and 16, Appendix B). Mr. Robert Comstock defined the path followed whereby a fine lamellar structure is transformed into a two-phase dispersion on high temperature exposure. The rationale for the structural evolution is similar to that advanced in previously ARO sponsored work (see publication 15, Appendix B). In brief, recrystallization takes place during high temperature exposure. This produces a "grain boundary grid" in the Nb lamellae. Subsequent thermal grooving along the grid results in pinching off of ellipsoidal particles which subsequently assume an approximately equiaxed shape. In the case of Cu-Nb, the equiaxed Nb particles restrict Cu grain growth, and the "equilibrium" structure consists of a Cu matrix with Nb particles situated at Cu grain boundaries.

Mr. Brian Murphy is investigating the Cu-NbC system (papers 9 and 19, Appendix B). The system is a prototypical nanocermet. Materials are synthesized by SPEX milling Cu-Nb mixtures to which either graphite or hexane is added. During milling the C (from the graphite or the organic)

reacts with Nb to form NbC.[3] The structures generated by such processing are nanocrystalline (Fig. 2). The materials coarsen during subsequent consolidation (at temperatures as low as 1273 K), but a nanocrystalline structure is still maintained. The hardnesses of these materials are impressive; for example, that of "pure" NbC is in the range of 1900 kgf/mm^2. A number of issues must be resolved to clarify the processing-structure-properties relationships in this system. First, using transmission electron microscopy (TEM), the morphology of the alloy microstructure must be clarified. Limited TEM studies to date indicate a nanoduplex structure (rather than one wherein Cu isolates the NbC phase) is formed. Iron contamination takes place due to mill abrasion during synthesis. To which phase(s) the Fe partitions is not known, nor is the response of the Fe on heat-treatment. As noted, this material can serve as a prototype of nanocermets. Much is known of the structure-property relationships in conventional (i.e., micro-) cermets. Thus, the results of this study can indicate the important differences and similarities between the properties of micro- and nanocermets.

We have also investigated heavy metal synthesis by MA. As described in publication 3 (Appendix B), MA through SPEX milling of Ni-W blends produces an amorphous FCC matrix in which nanocrystalline W particles are imbedded. Amorphization takes place only if the W content of the blend exceeds ca. 30 at. %. The presence of the hard W particles leads to mill abrasion (papers 3 and 4, Appendix B), thus producing a ternary Ni-W-Fe alloy. We have shown (publications 3 and 20) that essentially any composition within the Fe-Ni-W ternary triangle can be synthesized through adjustment of the initial alloy composition and control of the milling time.

The amorphous structure is not maintained during consolidation of processed powder. Crystallization products are a Ni rich (FCC) phase and an intermetallic compound. Depending on the initial composition the intermetallic is either isomorphous with NiW or Ni$_4$W. (Sometimes both compounds are crystallization products; the precise scenario depends on the processed powder composition). Iron is present in the intermetallics, and apparently stabilizes them (at least this is so for NiW). That is, although the Ni-W binary intermetallics are not stable above ca. 1373 K, we find that they persist for extended times at temperatures as high as 1473 K. As-consolidated structures have submicrometer structural scales. These can be contrasted to the tens of micrometers scale characteristic of heavy metals produced by liquid phase sintering. The hardnesses and compressive yield strengths of consolidated materials are high (Vicker's hardnesses are typically greater than 600 kg/mm^2 and compressive yield strengths are about 2 GPa for initially equiatomic Ni-W alloys). These strengths are much higher than those of conventional heavy metals, which are on the order of 1 GPa. We do not know whether the higher strengths derive from the fine scale or from the presence of the intermetallic. The latter, though, impairs ductility and toughness. Current efforts are

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3 - We note that NbC, the stochiometric form of which melts at ca. 4000 K, is synthesized at room temperature!
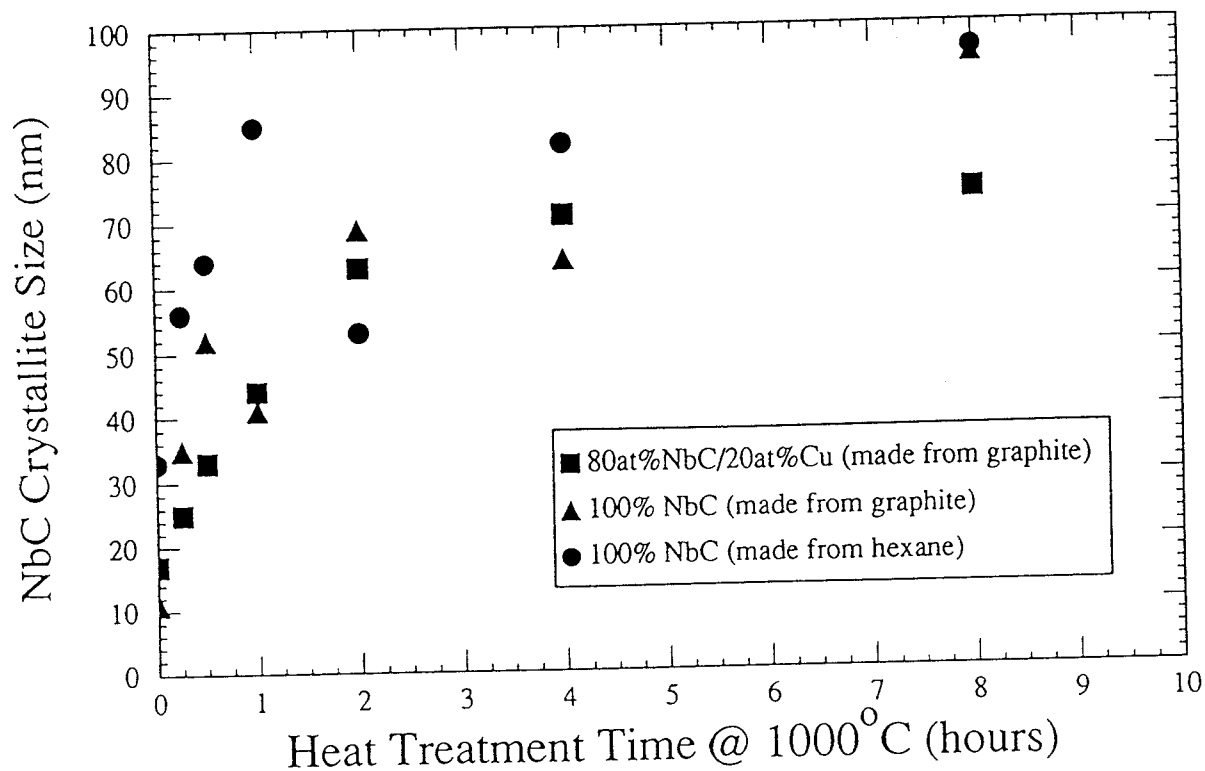
Figure 2: NbC crystallite size as a function of exposure time at 1273 K. Shown are x-ray crystallite sizes for as-synthesized powder (heat-treatment time of 0), for "quick hipped" powder (heat-treatment time of 1/4 hr) and for conventionally hipped powder (time=1 hr.) and for these materials after heat-treatment for extended times at the 1273 K. Consolidated structures slowly coarsen, but remain in the nanometer range even after extended thermal exposure at 1273 K.

concentrated on producing these materials by attrition milling. The lower power attritor will likely not lead to powder amorphization, but should generate a suitably fine scale material. We anticipate that intermetallic formation will not take place on consolidating powders produced in this manner because the intermetallic - a nonequilibrium crystallization product - forms as a result of decomposition of the even less stable amorphous phase.

Mr. Charles Mukira has conducted a thorough study of the compositions of the phases present, their amounts and their scales following consolidation and subsequent heat-treatment (paper 20, Appendix B). This work provides a basis for comparison of attritor and SPEX milled powders, both prior and subsequent to, consolidation, and also a means for comparison of these materials with conventional heavy metal alloys.

APPENDIX A: STUDENTS SUPPORTED AND DEGREES GRANTED; JULY 1, 1991-1994

Beverly J. M. Aikin, Ph. D., University of Virginia, 1992
David Maurice, Ph. D., University of Virginia, 1992[1]
Robert R. Vance, M. S., University of Virginia, 1991
Zhongang Wang, M. S., University of Virginia, 1992
Robert J. Comstock, Jr., M. S., University of Virginia, 1993[2]
Charles G. Mukira, Ph.D., Michigan Technological University, (in progress)
Brian R. Murphy, Ph.D., Michigan Technological University, (in progress)
Timothy M. Cook, M.S., Michigan Technological University, 1994

APPENDIX B: PUBLICATIONS; JULY 1, 1991 TO PRESENT

A. Archival Journals (in print)

1. R. R. Vance and T. H. Courtney, "Hot Isostatic Pressing of Mechanically Alloyed Cu-Nb Powders", Scripta Metall. et Mater., vol. 26, 1435, (1992)

2. T. H. Courtney and Z. Wang, "Grinding Media Wear During Mechanical Alloying of Ni-W Alloys in a SPEX Mill", Scripta Metall. et Mater., vol. 27, 777, (1992)

3. A. O. Aning, Z. Wang and T. H. Courtney, "Tungsten Solution Kinetics and Amorphization of Nickel in Mechanically Alloyed Ni-W Alloys", Acta Metall. et Mater., vol. 41, 165, (1993)[1]

4. R. W. Rydin, D. Maurice and T. H. Courtney, "Milling Dynamics: I. Attritor Dynamics: Results of a Cinematographic Study", Metall. Trans. A, vol. 24A, 175, (1993)[1]

5. T. Kosmac, D. Maurice and T. H. Courtney, "Synthesis of Nickel Sulfides by Mechanical Alloying", J. Am. Cer. Soc., vol. 76, 2345, (1993)[1]

6. B. J. M. Aikin and T. H. Courtney, "The Kinetics of Composite Particle Formation During Mechanical Alloying", Metall. Trans. A, vol. 24A, 647, (1993)

7. B. J. M. Aikin and T. H. Courtney, "Modeling of Particle Size Evolution During Mechanical Alloying", Metall. Trans. A., vol. 24A, 2465, (1993)

8. D. Maurice and T. H. Courtney, "Modeling of Mechanical Alloying: I. Deformation, Coalescence and Fragmentation Mechanisms", Metall. and Mater. Trans. A, vol. 25A, 147, (1994)[1]

9. B. R. Murphy and T. H. Courtney, "Synthesis of Cu-NbC Nanocomposites by Mechanical Alloying", *Nano*Structured Mater., vol. 4, 365, (1994)

B. Archival Journals (in press or submitted)

10. R. J. Comstock, Jr. and T. H. Courtney, "Elevated Temperature Stability of Mechanically Alloyed Cu-Nb Powders", to be published in Metall. and Mater. Trans. A [2]

11. T. H. Courtney, "Modeling of Mechanical Milling and Mechanical Alloying", to be published in Reviews in Particulate Materials [3]

12. T. H. Courtney and D. Maurice, "Process Modeling of the Mechanics of Mechanical Alloying", to be published in Scripta Metall. et Mater. (Overview Set)[3]

13. D. Maurice and T. H. Courtney, "Modeling of Mechanical Alloying: II. Development of Computational Programs", submitted for publication [1]

14. D. Maurice and T. H. Courtney, "Modeling of Mechanical Alloying: III. Applications of Computational Programs", submitted for publication[1]

C. Refereed Proceedgins and Conference Publications

15. T. H. Courtney, "Elevated Temperature Morphological Instabilities in Metal Matrix Composites", *Metal Matrix Composites - Orocessing, Microstructure and Properties, Proc. 121th Riso Intl. Symposium on Materials Science*, ed. N. Hansen, D. Juul Jensen, T. Leffers, H. Lilholt, T. Lorentzen, A. S. Pedersen, O. B. Pedersen and B. Ralph, Riso National Laboratory, Roskilde, Denmark, 17, (1991)[3]

16. T. H. Courtney and R. J. Comstock, Jr, "Elevated Temperature Stability of Lamellar Structures with Specific Application to Mechanically Alloyed Powders", *Modeling of Coarsening and Grain Growth*, ed. S. P. Marsh and C. S. Pande, TMS, Warrendale, Pa., 71, (1993)[3]

17. T. H. Courtney, D. Maurice, B. J. M. Aikin, R. W. Rydin and T. Kosmac, "Local and Global Modeling of Mechanical Alloying", *Proc. 2nd Intl. Conf. on Structural Applications of Mechanical Alloying*, ed. J. J. deBarbadillo, R. Schwarz and F. H. Froes, ASM International, Materials Park, O., 1, (1993)[1]

18. D. Maurice and T. H. Courtney, "Modeling of Mechanical Alloying", JOM, vol. 44(8), 10, (1992)[1,3]

D. Refereed Proceedings and Conference Publications (In Press or Submitted)

19. T. H. Courtney, "In Situ Processing of Metal Matrix Composites", to be published in *Proc. 8th CIMTEC-World Ceramics Congress and Forum on New Materials*, Florence, Italy (1994)[3]

20. B. R. Murphy and T. H. Courtney, "Structure-Property-Processing Relationships in Nanocrystalline and Fine-Grained NbC and Cu-NbC Composites", to be published in *Proc. Intl. Symposium on Synthesis and Processing of Advanced Materials*, Chicago, Ill (1994)

21. C. G. Mukira and T. H. Courtney, "The Structure and Properties of Mechanically Alloyed and Consolidated Ni-W(Fe) Alloys", to be published in *Proc. Intl. Conf. on Tungsten and Refractory Metals*, Washington,D.C., (1994)

1 - Partial support from DARPA/NASA
2- Indicates support from AASERT supplement to grant
3 - Indicates invited lecture/paper